

Surface Film Formation of Graphite Negative Electrodes in Rechargeable Lithium Batteries

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It is generally accepted that stable surface film is formed on graphite negative electrodes in rechargeable lithium batteries upon the first charging and thereby the graphite surface is passivated against solvent decomposition. The film is called “solid electrolyte interface” (SEI), which is conductive for lithium-ion, but does not have electronic conductivity. Hence the film suppresses further solvent decomposition, but through this film lithium ion can be intercalated within graphite. However, much of SEI formation has not been fully clarified yet in spite of its importance in the battery reactions.

We have so far investigated the mechanism for the surface film formation using electrochemical scanning tunneling microscopy [EC-STM] [1,2] and found that the intercalation of solvated lithium ions plays a key role in the initial stage of surface film formation at around 1 V vs. Li/Li⁺. In the present study, we use electrochemical atomic force microscopy (EC-AFM) and report the morphology changes at lower potentials down to 0 V.

Surface morphology changes were observed with an AFM system (Molecular Imaging, PicoSPM), which was placed in argon-filled glove boxes with dew points < −60°C. Highly oriented pyrolytic graphite (HOPG, Advanced Ceramics, ZYH) blocks were used as test electrodes for AFM observation.

Slow scan cyclic voltammetry (CV) at 0.5 mV s^{−1} was carried out, and surface morphology changes during CV were observed by EC-AFM. Panel (a) in Fig. 1 shows CVs of HOPG in 1 M LiClO₄/EC+DEC. Cathodic peaks were observed at 1.0, 0.8, and 0.5 V, and large cathodic current rose at potentials more negative than 0.3 V. The three cathodic peaks are related to solvent decomposition and SEI formation because they disappeared in the second cycle. Figure 1(b) shows an AFM image obtained in the potential range of 0.95–0.80 V during CV in Fig. 1(a). Many atomically flat parts raised by 1 or 2 nm appeared. We also reported the formation of similar features, called “hill-like structures”, at around 1 V in our previous reports using STM [1,2], and we suggested that the intercalation of solvated lithium ions for the formation of the hill-like structures [6,7]. The hills observed in Fig. 1(b) overlap with one another so that the pattern made by hill formation is very complicated.

At potentials lower than 0.65 V, particle-like substances were precipitated on the basal-plane surface. The number of the precipitates increased with lowering the potential down to 0.0 V. However, at 2.8 V after the reverse sweep, the precipitates disappeared almost completely. Figure 1(c) shows the AFM image of an extended area (10 × 10 μm) including the 5 × 5 μm area observed during CV. Many precipitates are seen on the surface outside the 5 × 5 μm area, although they are missing inside the 5 × 5 μm area. Hence repeated scanning with the tip during the reverse CV sweep to 2.8 V scraped off the precipitates formed on the 5 × 5 μm area. The thickness of the precipitate layer in Fig. 1(c) was about 40 nm. These precipitates are considered to be a kind of polymer formed by decomposition of EC, as reported in a previous report using Pyro/GC/MS analysis

[3], and to suppress further solvent decomposition on the basal plane of graphite.

In a similar manner, AFM images were obtained during the second cycle of CV. The structure formed by co-intercalation of solvents and the following decomposition beneath the surface did not change during the second cycle; however, the thickness of the precipitate layer on the basal-plane surface increased to 70 nm after the second cycle. These facts indicate that the intercalation of solvated lithium ion was terminated during the cathodic sweep of the first cycle, whereas the SEI layer on the basal plane grew continually in the second cycle.

References

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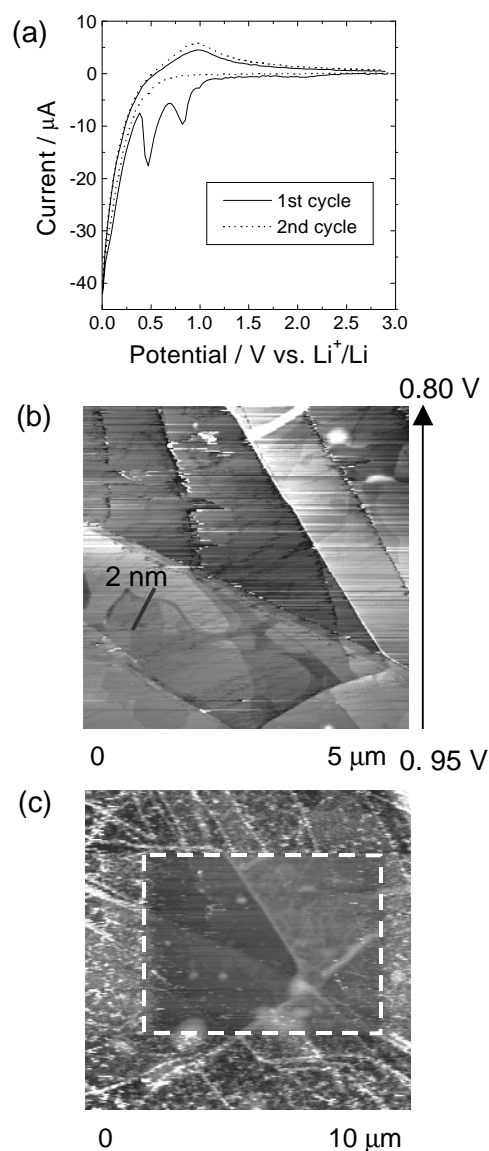


Fig. 1. (a) CV on HOPG (1.2 cm²) in 1 M LiClO₄/EC+DEC at 0.5 mV s^{−1}. (b) EC-AFM images of HOPG basal plane obtained (b) in the range of 0.95–0.80 V during the first CV and (c) at 2.8 V after CV. Dotted square in (c) shows the area (5 × 5 μm) scanned with the cantilever during CV.

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